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PAPER NO. 55

**INTRODUCTION TO EXIDE CORPORATION'S  
HIGH TEMPERATURE METALS RECOVERY SYSTEM**

**Presented At:**

**International Symposium on Environmental Technologies**

**Plasma Systems and Applications**

**October 8-11, 1995, Atlanta, Georgia**

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**PAPER TO BE PRESENTED AT GEORGIA UNIVERSITY OF TECHNOLOGY**

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**1. INTRODUCTION**

Environmental strategies concerning the processing and ultimate fate of wastes and byproducts are of ever increasing importance to the public and business sectors in the world today. Recycling materials and reusing energy from wastes and byproducts results in a reduction of environmental impacts and the cost of disposal. These are the key steps in reaching the ultimate goal of waste minimization.

Waste treatment and disposal can create a negative financial and liability impact on the operations of industries that generate waste. Additional resource needs are costs associated with handling currently generated wastes, financial assurances, and recordkeeping necessary to bring generators into compliance with current and future environmental regulations. In the United States, the secondary impact occurs if historical treatment and disposal results in a Superfund liability to a generator. The generator may, at a later date, be required to retreat and dispose of historical waste.

In response to these needs, Exide Corporation, in its vision to develop waste minimization programs, has developed the Exide High Temperature Metals Recovery (EHTMR) process. This process can treat a variety of wastes and byproducts where metals contents are an issue, recover the metal values for reuse, and produce a metals-depleted slag that can be marketable under the most stringent proposed EPA regulations for leachability of contaminants. The central feature of the EHTMR process is the

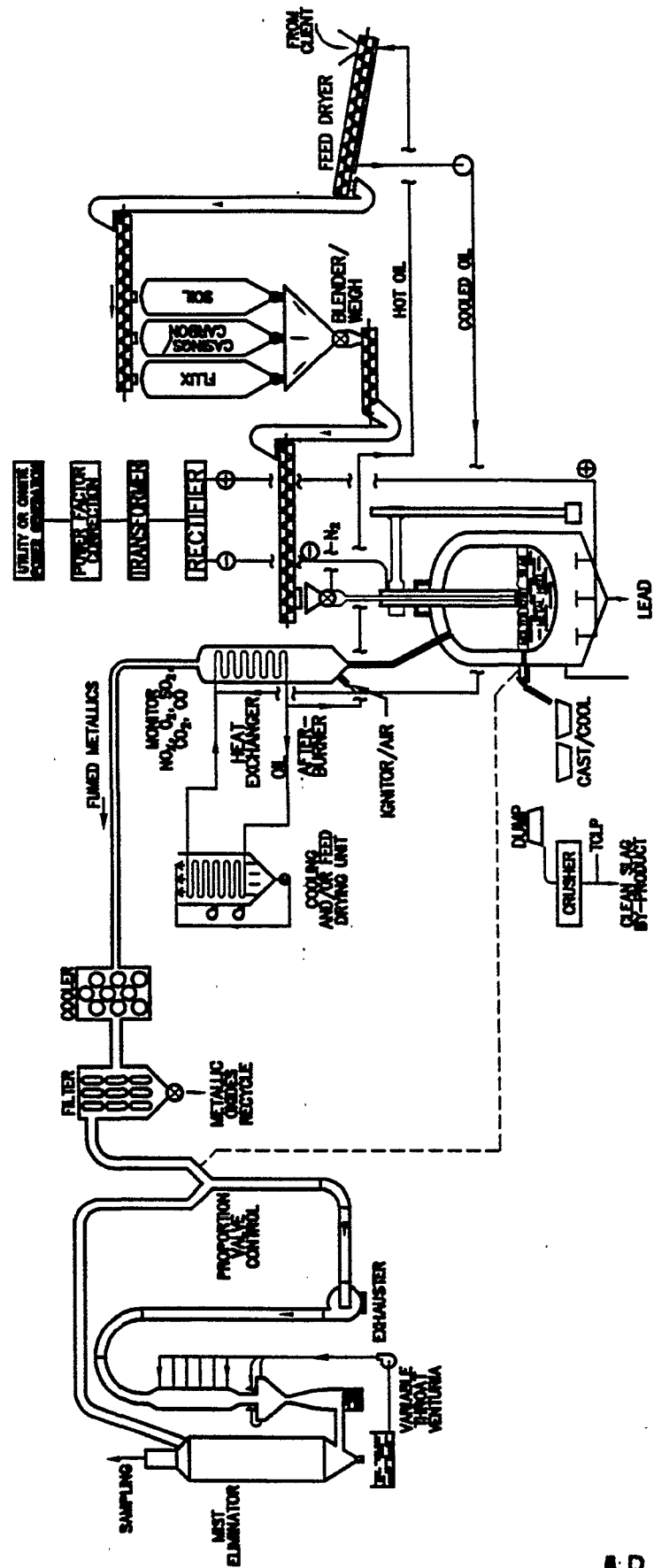
exposure of treated materials to a transferred arc plasma generated in an electric furnace. The process achieves a reduction in costs and liability by recovering portions of a waste that can be recycled or reclaimed and produces a slag that has beneficial use to society.

## **2. PROCESS DESCRIPTION**

While the EHTMR process can deal with materials containing a wide variety of chemical or physical contaminants, the initial focus in this study has been on contaminated wastes soil from past lead or battery recycling operations. The materials present at this type of site, include soil, heavy metals (including lead and lead compounds ( $\text{PbO}$ ,  $\text{PbSO}_4$ )) and battery case materials (plastic and rubber) which contain appreciable amounts of carbon compounds.

The primary goals of process development have been to permanently remove undesirable constituents including metals from contaminated substrates (soils, slags, etc.), to recover the metals for reuse, recover thermal and chemical energy, and to render process byproducts (slag) with the lowest residual metals contents achievable that pass the most stringent Toxic Characteristic Leaching Procedure (TCLP). In the case of soil contaminated with lead (heavy metals and especially lead), maximum removal of lead in the process is achieved.

Lead, along with several other heavy metals present with naturally-occurring lead, exhibits an elevated vapor pressure at temperatures achievable in metallurgical furnaces ( $> 2500^\circ\text{F}$ ). Optimization of vaporization to separate metals, a practice known as "slag fuming", has been used by the lead and zinc industries extensively to recover metal values from byproducts such as heavy metals compounds and furnace slags.



# STAND ALONE SYSTEM

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Slag fuming has been in use by the lead industry for approximately 70 years. Typically, the primary purpose has been to recover zinc from blast furnace slags in primary lead production<sup>1,2</sup>. Lead is also removed in the fuming process, and the utilization of this principle is central to the operation of the EHTMR process. If lead is concentrated in the furnace, it can also be removed in its metallic phase.

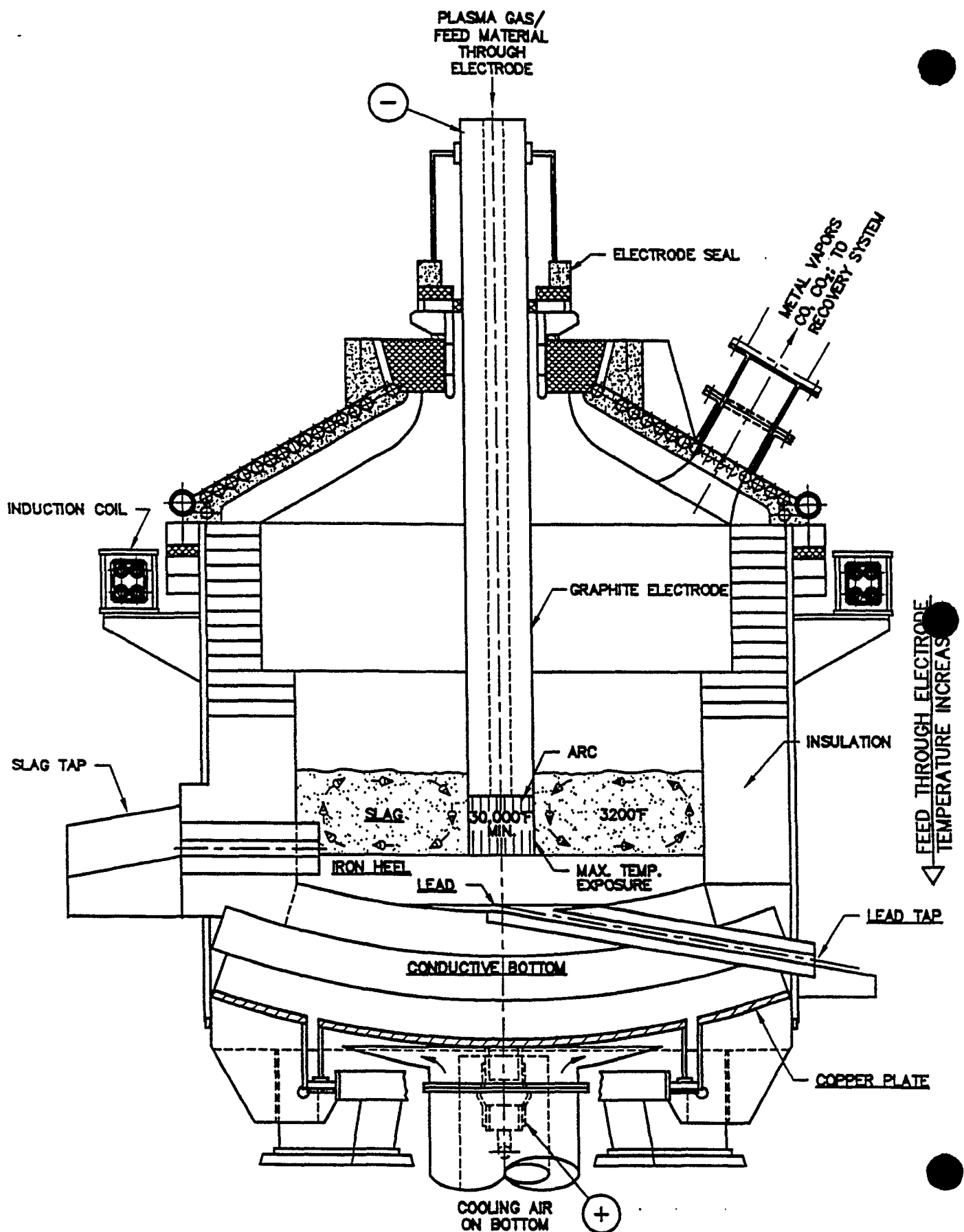
The EHTMR process, shown in Figure 1, can be summarized as an assembly of three subsystems:

1. Solids preparation, storage, and feeding.
2. Metallurgical furnace capable of providing optimized fuming conditions, operated in a transferred plasma arc mode.
3. Offgas handling system for fume condensation and solids removal, gas cleaning, and offgas utilization for energy.

The system can be designed and built as modules for transporting by trailer with minimal mobilization and demobilization.

The key component is the metallurgical furnace, which must provide optimum metals partitioning and separation. Commercial slag fuming furnaces have traditionally used coal as the primary energy source. Bath temperatures employed typically range to 1,400°C (2,552°F). Modelling work concerning coal fired slag fuming processes had shown that gas flow through slag baths influenced fuming rates at these temperatures<sup>3</sup>. As minimization of process offgas requirements has been a goal of the EHTMR process developments, it was felt that the process would require higher temperatures to compensate for the lack of gas flow through the bath.

FIGURE 2



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Electric furnaces have been employed for metallurgical operations involving crushed ores, at temperatures as high as  $1,700^{\circ}\text{C}$  <sup>4</sup> ( $3,092^{\circ}\text{F}$ ). This and the comparatively low offgas generation rates inherent in electric furnace operation are the rationale behind the use of an electric furnace for the EHTMR process.

The heart of the EHTMR system is a D.C. electric plasma arc furnace; offered by Asea Brown Boveri (ABB), shown in Figure 2. This furnace features a hollow graphite electrode through which solids can be fed, and a cathode assembly that includes a conducting graphite furnace bottom in contact with a liquid metal heel. In order to assist in solids feeding and to provide arc stabilization, the system is equipped with a system to feed inert plasma gas through the electrode. Feeding solids requiring fuming through the electrode requires their passage through the zone of maximum energy density at the arc (Figure 3) which enhances volatilization of metals. This is an advantage inherent in transferred plasma arc operations with a hollow electrode feed, which is not possible in non-transferred plasma arc operations.

It should be noted that all of the components of the EHTMR system are commercially proven in metallurgical service. As such, technical risks inherent in "innovative" processing of liquid metals or molten baths are not found in the EHTMR process.

The balance of plant equipment for the EHTMR process includes solids preparation equipment for crushing, drying, and feeding solids. Gas handling equipment includes solids separation (bag filtration), gas cleaning, chemical energy utilization and/or afterburning as required. The process can generate offgas that contains significant

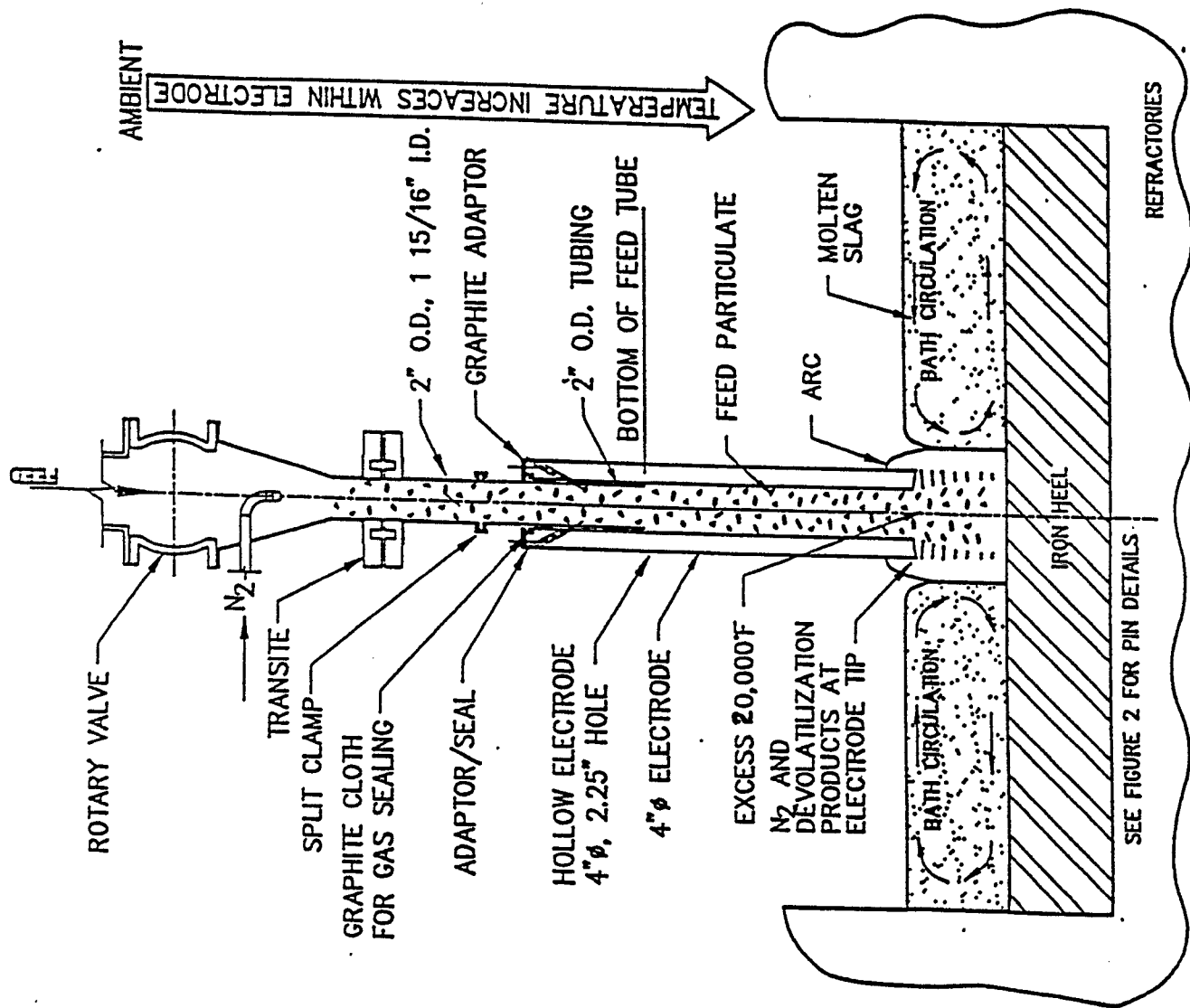


FIGURE 3  
PRINCIPLES OF OPERATION

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quantities of  $H_2$  and  $CO$ , and can be used to produce methanol or chemicals.

As the initial application of the EHTMR process is for lead fuming, reducing conditions are to be maintained. The reducing agent for the process is composed of ground battery cases. The furnace is sealed, allowing close control of furnace gas composition. This also permits control of the system Post Combustion Ratio (PCR), and PCR optimization can assist in optimizing the energy release from partial combustion of battery cases. Thus, in addition to maintaining a reducing atmosphere, the addition of an excess of reducing agent can offset a portion of the system electric power consumption with chemical energy. The principle of offsetting electric energy with chemical energy has received a good deal of attention in electric furnace steel making<sup>5</sup>. In the case of the EHTMR process, this serves to reduce operating costs.

In addition to removing solids through fuming, the EHTMR process can reduce certain elements from the slag phase, such as iron. A reduced furnace atmosphere causes these elements to partition from the slag phase to the liquid metal heel. This can serve to reduce the amount of furnace slag produced, or aid in the recovery and resale of metal values.

### **3. PILOT TEST RESULTS**

#### **3.1 Objective of Pilot Tests**

Pilot testing for the EHTMR process has been carried out as part of the commercial development program. Included in the pilot testing work was the design of a pilot arc furnace by ABB and Exide personnel, and the installation of offgas monitoring equipment for assistance in evaluating furnace conditions and

measuring post combustion ratios.

The goal of pilot testing was to process soil with a lead content of 3 wt.%, under conditions anticipated from commercial operation. A variety of conditions were to be evaluated to determine conditions that would maximize lead removal through fuming, and minimize the residual lead content of the furnace slag.

### **3.2 Materials Treated**

Pilot testing for the process has focused on materials from a site of a former battery recycling operation. This site includes soil that is contaminated with lead and lead compounds. Also found at the site are broken rubber battery cases. The objective of pilot testing has been to demonstrate the removal of lead from the soil through fuming, using the battery cases as a reducing agent, as well as a supplemental energy source.

Table 1 shows the composition of the soil found at the site. The high silicon dioxide content and the relatively low levels of flux (MgO, CaO, Fe compounds) could be expected to produce an acidic and possibly refractory slag. As such, the decision was made to add calcined lime as a flux.

Table 2 shows a proximate analysis of rubber battery cases used for the pilot tests. The carbon content is indicative of the suitability of the material as a metallurgical reducing agent.

| TABLE 1                   |                  |                                |      |      |                   |                  |                                |
|---------------------------|------------------|--------------------------------|------|------|-------------------|------------------|--------------------------------|
| CHEMICAL ANALYSIS OF SOIL |                  |                                |      |      |                   |                  |                                |
|                           | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> |
| WT %                      | 60.0             | 7.83                           | 2.38 | 1.15 | 0.70              | 4.09             | 17.9                           |
|                           |                  |                                |      |      |                   |                  |                                |
|                           | Si               | Fe                             | Mg   | Ca   | Na                | K                | Al                             |
| WT %                      | 28.0             | 5.48                           | 1.44 | 0.82 | 0.52              | 3.40             | 9.47                           |
| Source Laboratory #2      |                  |                                |      |      |                   |                  |                                |

| TABLE 2                                    |           |
|--|-----------|
| PROXIMATE ANALYSIS OF GROUND BATTERY CASES |           |
| Moisture                                   | 1.7 WT %  |
| Volatile Matter                            | 28.2 WT % |
| Ash  | 18.1 WT % |
| Fixed Carbon                               | 52.0 WT % |
| Sulfur                                     | 2.5 WT %  |

| TABLE 3  |          |
|--|----------|
| LEAD CONTENTS OF MATERIALS<br>FED TO EHTMR FURNACE |          |
| TEST   | WT. % Pb |
| 1  | 3.1      |
| 2  | 3.2      |
| 3  | 3.0      |
| 4  | 2.7      |
| 5  | 3.4      |
| 6  | 1.6      |
| 7  | 3.1      |
| 8  | 3.1      |

During pilot testing a total of 1118 kg. of material was processed in the pilot furnace in a total of 12 heats. In each case, lead sulfate was blended with dried, 6 mm x 0 soil, with the objective lead content of 3 wt. %. Table 3 shows the lead content of the feed material for each test.

### 3.3 Pilot Test Equipment

As mentioned, construction of a pilot furnace was included in the scope of pilot testing. This furnace system was connected to a power supply capable of applying 250 kw. of electric energy to the furnace.

Solids, which included 6 mm x 0 ground battery cases, were fed through the hollow electrode, as seen in the pilot plant diagram (Figure 3). Also fed through the electrode was nitrogen gas. The percentage of battery cases in the feed was varied to provide a variety of furnace atmospheres.

The offgas system included an afterburner and a water only scrubber system. Furnace offgas was sampled ahead of the afterburner. Analytical equipment was maintained on site to measure  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  contents in the offgas. Additionally, "bag" gas samples were taken and sent offsite for  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  composition analyses.

### 3.4 Test Results

As mentioned, a total of 12 heats were conducted for pilot testing. Feed rates of ground battery cases were varied, while feed rates of soil and lead were constant. For this paper, the heats have been grouped into 8 tests.

The first campaign was conducted using oxidizing conditions in the furnace, to debug equipment. The second campaign featured significant additions of ground battery cases, to provide a reducing atmosphere and to evaluate offgas characteristics for full-scale design requirements. In all, 8 tests were conducted.

The primary objective of the EHTMR program is to produce a furnace product (slag) with a minimum lead content. While the feed materials contained 3% Pb, slags produced were consistently below 100 ppm mg as seen in Table 4. Elimination of lead from the slag, based on feed and slag material balances, is also presented for each test in Table 4. Lead removal rates in each case exceed 99.56%, with the highest value at 99.94% elimination. As seen in Table 5, measured bath temperatures were in the range of the boiling temperature of lead, and the use of the high temperatures found in the plasma furnace helped maximize lead elimination.

| TABLE 4            |                   |
|--------------------|-------------------|
| LEAD REMOVAL RATES |                   |
| HEAT               | % OF LEAD REMOVAL |
| 1                  | 99.83             |
| 2                  | 99.56             |
| 3                  | 99.90             |
| 4                  | 99.86             |
| 5                  | 99.93             |
| 6                  | 99.62             |
| 7                  | 99.96             |
| 8                  | 99.98             |

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For comparison, Table 6 shows the residual lead content of EHTMR slag with those measured for commercial slag fuming processes. As seen, the residual lead content of EHTMR slag (19.0 mg/kg) is much lower than those of tail slags from other fuming processes (300-3,800 mg/kg).

In order to maximize the commercial value of the HTMR process, it is desirable to produce a fume (offgas solids) with an elevated lead content. As seen in Table 7, the lead levels of commercially produced fume are within the range found in EHTMR pilot testing.

When run under oxidizing conditions, the process slag was found to be enriched in iron and magnesium over the feed soil, as seen in Table 8. This was attributed to attack on magnesium oxide refractory by the high silica content slag.

| TABLE 5   |                     |   |
|---|---------------------|---|
| MEASURED BATH TEMPERATURES<br>FOR EHTMR PILOT TESTING |                     |   |
| Test  | Bath Temperature °C | Lead Vapor Pressure, ATM<br>of Measured Temperature |
| 1   | 1601                | 0.45  |
| 2   | 1756                | > 1.0   |
| 3   | 1760                | > 1.0   |
| 4   | 1751                | > 1.0   |
| 5   | 1747                | > 1.0   |
| 6   | 1542                | 0.31  |
| 7   | 1763                | > 1.0   |
| 8   | 1755                | > 1.0   |

| TABLE 6  |       |         |         |         |         |         |
|--|-------|---------|---------|---------|---------|---------|
| COMPARISON OF INPUT AND SLAG PB CONTENTS<br>FOR EHTMR PROCESS AND COMMERCIAL SLAG FUMING PROCESSES |       |         |         |         |         |         |
| Process  | EHTMR | Ref. 1* | Ref. 2* | Ref. 6* | Ref. 7* | Ref. 8* |
| Input Pb<br>WT %   | 3.0   | 2.5     | 2.6     | 2.3     | 2.9     | 2.0     |
| Treated<br>Slag<br>mg Pb/kg  | 19.0  | 500     | 300     | 3,800   | 460     | 1,800   |
| * Commercial slag fuming process   |       |         |         |         |         |         |



| TABLE 7   |        |         |         |            |
|---|--------|---------|---------|------------|
| COMPARISON OF FUME LEAD CONTENTS,<br>EHTMR AND COMMERCIAL SLAG FUMING PROCESSES |        |         |         |            |
| Process   | EHTMR  | Ref. 1* | Ref. 2* | Ref. 8*    |
| WT % Pb<br>in Fume  | 3 - 29 | 9.8     | 12.5    | 6.0 - 12.8 |
| * Commercial slag fuming process  |        |         |         |            |

| TABLE 8  |                  |                                |      |      |                                |
|--|------------------|--------------------------------|------|------|--------------------------------|
| COMPARISON OF SOIL AND SLAG COMPOSITIONS,<br>FURNACE RUN UNDER OXIDIZING CONDITIONS  |                  |                                |      |      |                                |
| WT %   | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO  | CaO  | Al <sub>2</sub> O <sub>3</sub> |
| Soil   | 60.0             | 7.83                           | 2.35 | 1.15 | 17.9                           |
| Slag   | 35.2             | 33.9                           | 16.7 | 1.41 | 12.2                           |
| NOTE: Tests resulted in pickup of 51 kg Iron (as Fe <sub>2</sub> O <sub>3</sub> ) from anode<br>and 40 kg MgO from furnace refractory. |                  |                                |      |      |                                |

While the use of an oxidizing atmosphere may cause iron oxide pickup by the slag, the reverse was true for operation under reducing conditions. Data from material balances on soil and slags, presented in Table 9, suggest the reduction of iron oxides in the slag to neutral metal. For treatment of materials with significant iron contents in the EHTMR process, the production of pig iron as a byproduct can provide an economic credit, and reduce byproduct slag volumes.

The attack by the slag on the magnesium oxide refractory was lessened by the use of a reducing atmosphere, as seen in Table 10. This may have been due to the presence of a larger liquid iron anode in the furnace under reducing conditions, protecting a larger proportion at the magnesium oxide refractory.

As mentioned, furnace offgas compositions were measured, and a selection can be found in Table 11. Under oxidizing conditions,  $\text{CO}_2$  found in the offgas was probably due to electrode combustion. Reducing conditions found CO contents to range from 15-30% typically, although under some conditions, offgas CO contents as high as 45+% have been encountered.

Offgas compositions were used to estimate release of chemical energy in the system. This was done by calculation using heats of combustion and carbon monoxide and carbon dioxide contents of the offgas. This was done for approximation purposes, no effort was made to assess the effects of endothermic reactions with bath constituents (i.e., iron oxide reductions) or the water gas reaction.

| TABLE 9                            |         |                      |            |              |            |                 |  |
|------------------------------------|---------|----------------------|------------|--------------|------------|-----------------|--|
| IRON BALANCES, REDUCING CONDITIONS |         |                      |            |              |            |                 |  |
| TEST                               | OFFGAS  |                      | SOIL       |              | SLAG       |                 | %<br>REDUCTION<br>OF IRON<br>FROM SLAG |
|                                    | %<br>CO | %<br>CO <sub>2</sub> | WT %<br>Fe | Kg Fe<br>Fed | WT %<br>Fe | Kg Fe<br>Tapped |  |
| 6                                  | 15      | 9                    | 5.5        | 2.4          | 1.0        | 0.5             | 79                                     |
| 7                                  | 15      | 9                    | 5.5        | 9.0          | 1.4        | 3.5             | 61                                     |
| 8                                  | 29      | 3                    | 5.5        | 7.0          | 0.1        | 0.2             | 97                                     |

| TABLE 10  |                             |                             |                               |
|---|-----------------------------|-----------------------------|-------------------------------|
| EFFECT OF FURNACE ATMOSPHERE ON<br>MgO REFRACTORY CONSUMPTION |                             |                             |                               |
| Test  | kg MgO<br>Pickup by<br>Slag | MgO<br>Consumption<br>kg/hr | Furnace<br>Atmosphere         |
| 4   | 40.3                        | 7.5                         | Oxidizing, 16% O <sub>2</sub> |
| 6   | 0.73                        | 0.88                        | Reducing, 8% CO               |
| 7   | 0.68                        | 0.09                        | Reducing, 15% CO              |
| 8   | 8.0                         | 1.0                         | Reducing, 29% CO              |

| TABLE 11                            |                    |                |      |                 |                |                |                  |
|-------------------------------------|--------------------|----------------|------|-----------------|----------------|----------------|------------------|
| FURNACE OFFGAS COMPOSITIONS, % VOL. |                    |                |      |                 |                |                |                  |
| Test                                | Furnace Atmosphere | O <sub>2</sub> | CO   | CO <sub>2</sub> | N <sub>2</sub> | H <sub>2</sub> | H <sub>2</sub> O |
| 1 & 2 Average                       | Oxidizing          | 16.1           | 0.03 | 4.0             | *              | *              | *                |
| 3 & 4 Average                       | Oxidizing          | 16.3           | 0.03 | 4.0             | *              | *              | *                |
| 6                                   | Reducing           | 0.12           | 14.1 | 10.1            | *              | *              | *                |
| 7                                   | Reducing           | 0.21           | 14.8 | 9.3             | *              | *              | *                |
| 8                                   | Reducing           | *              | 28.7 | 2.6             | 50.6           | 11.6           | 6.4              |
| * Not determined                    |                    |                |      |                 |                |                |                  |

These data, along with electrical energy input rates and post combustion ratios (PCR) are shown in Table 12. As seen, the release of chemical energy in the system can make a significant contribution to system energy requirements. Additionally, the chemical energy contained in the offgas can be significant. The PCR can be adjusted to provide a balance, as required, between chemical energy released in the furnace and chemical energy in the offgas.

TABLE 12

**OFFGAS COMPOSITION, ENERGY RELEASED IN FURNACE,  
AND EFFECT ON POST COMBUSTION RATIO (PCR)**

**TEST 8**

$$\text{PCR} = \frac{(\text{H}_2\text{O}) + (\text{CO}_2)}{(\text{H}_2\text{O}) + (\text{H}_2) + (\text{CO}_2) + (\text{CO})}$$

| Bath Sample                         | A       | B       | C       |
|-------------------------------------|---------|---------|---------|
| Offgas % CO                         | 11.9    | 22.9    | 28.7    |
| % CO <sub>2</sub>                   | 8.5     | 3.8     | 2.6     |
| % H <sub>2</sub> O                  | 4.7     | 5.3     | 6.4     |
| % H <sub>2</sub>                    | 5.2     | 7.0     | 11.6    |
| PCR                                 | 0.44    | 0.23    | 0.18    |
| Electric Energy Input               | 175 kw  | 160 kw  | 166 kw  |
| Chemical Energy Released in Furnace | 102 kw  | 71.7 kw | 67.8 kw |
| Sensible Energy in Offgas           | 40.3 kw | 29.2 kw | 27.1 kw |
| Chemical Energy in Offgas           | 104 kw  | 151 kw  | 183 kw  |

#### 4. CONCLUSIONS

The EHTMR process has been tested in pilot scale, to provide performance information required to take the process to commercial scale. From these tests, the following conclusions have been drawn:

1. While the 3 wt. % lead in feed materials was comparable to the lead content of lead blast furnace slags subjected to commercial fuming, the residual lead contents (19-95 mg/kg) of EHTMR slag were much lower than those from current slag fuming practice (300 - 3800 mg/kg).
2. Bath temperatures maintained were typically over 1,740°C, in the vicinity of the boiling point of lead. This produced lead elimination rates ranging from 99.56 to 99.94 wt %.
3. Lead content of the offgas solids ranged from 3 - 29 wt % and typically exceeded 8.6 wt %.
4. Iron oxides present in the soil could be reduced to iron metal, raising the possibility of pig iron as EHTMR byproduct.
5. The partial combustion of the reducing agent (ground battery cases) could furnish a substantial portion of the required process energy, offsetting more expensive electric energy.
6. The use of a transferred arc plasma furnace for the EHTMR process provides a high level of performance and economy for treating materials at Superfund sites.

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